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EFFECT OF CATHODIC HYDROGEN CHARGING ON THE SURFACE OF DUPLEX STAINLESS STEEL

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Introduction

The effect of cathodic hydrogen charging on the mechanical properties of steels has been extensively investigated (1-5). There is a general agreement, that cathodic charging during a tensile test leads to reduction in ductility, and embrittlement (5-7). The effects of cathodic charging on the surface of metals also have been reported in the literature. Electrochemical hydrogen charging of austenitic stainless steels has been shown to result in surface cracks even without externally applied strain/stress (8). So far no quantitative analysis of the surface strains has been reported. The aim of this investigation is to study the effect of cathodic charging on the surface of duplex stainless steel and to estimate the plastic deformation of the surface layer using computer simulation.

Experimental

The material investigated was commercially available duplex stainless steel with a chemical composition given in table I

TABLE
I: Chemical composition of duplex stainless steel

C	Cr	Ni	Mo	N	S	P	Fe
<0.02	22	5.6	2.3	0.14	<0.02	<0.02	bal

The material is a 10 mm thick, hot rolled plate, solution annealed and water quenched. A strip 100 X 10 X 1.1 mm was cut with electro discharge machining, perpendicular to the rolling direction through the thickness. The surfaces of the specimen were ground with 1000 grit paper. The surfaces were further electro-polished to remove the deformed surface layer from the mechanical polishing operation. The final dimensions of the specimen were 100 X 10 X 1 mm. One surface of the specimen was coated with a thin coat of insulating lacquer. The other surface was left in the polished state. One end of the specimen was anchored in polymer and was connected to an electrical lead. The anchored specimen with the electrical lead was then immersed in a baker filled with 1N H_2SO_4 with 0.25 g/l Na_2SO_4. The specimen was placed vertically with the free top end of the specimen level with the elctrolyte surface. A platinum electrode was used as an anode and the specimen was connected to a DC power supply as a cathode. A current density of 0.1A/cm^2 was maintained. The duration of charging was 8 hours.

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The deflection of the free end of the specimen was monitored during the charging experiment with a travelling microscope. After charging, the specimen was cleaned and dried, and was allowed to out gas in air for 72 hrs at room temperature. It was then prepared for SEM examination.

The residual stresses were measured with X-ray diffraction applying the $\sin^2 \Psi$ method using a computerised residual stress measurement system.

Computer Simulation

The stresses generated by cathodic hydrogen charging were estimated using computer modeling using the finite element method. It was assumed that the hydrogen concentration during charging was 60 %. The diffusion of hydrogen into the material was calculated. It was assumed that hydrogen introduces dilatation in the material. Based on the dilatation introduced by hydrogen, and using material properties, stresses on the surface were calculated. The coupling between dilatation due to the presence of hydrogen and the mechanical deformations was taken into account. The stresses were calculated using an elastic-plastic material model with isotropic hardening. The description of plastic deformation was based on the Von_Mises yield criterion and classical flow theory (8). The yield stress was assumed to be independent of the hydrogen concentration. Cracking of the material was also not taken into account.
For diffusion calculations, Fick's equation was used with constant diffusivity. The diffusion coefficient was assumed to be independent of stresses, and of hydrogen concentration. The diffusion equation and the equations, which describe the equilibrium of the stresses constitute a set of coupled nonlinear equations. Using Galerkin's method these equations were discretised according to the standard finite element procedure (9). The resulting system was solved for discrete time steps using Newton-Raphson iteration. The material properties used in the simulation are summarized in table II.

TABLE
II: Material Properties Used In Simulation

Diffusion coefficient of Hydrogen	: D = 2×10^{-15}m s^{-1}
Expansion coefficient due to Hydrogen,(lineal)	: α = 0.1 (Strain at 100 % concentration)
Young's modulus	: E = 210 GPa
Poissons ratio	: n = 0.3
Yield stress	: σ0.2 = 480 MPa
Initial hardening modulus (at yield stress)	: H = 2.9 GPa
Ultimate tensile stress	: σmax = 730 MPa

A surface concentration of 60 % H at a current density of 0.1 A/cm^2 was assumed. With nickel a dilatation of 6 % has been observed with a 60% H content (10). It is claimed that with cathodic hydrogen charging of AISI 304 stainless steels, a hydrogen induced phase is formed which has a lattice parameter approximately 5.2 % larger than the original lattice (11). For the simulations it is assumed that there is no phase change due to hydrogen charging. An expansion of 6 % with 60 % hydrogen concentration was assumed to apply also to duplex stainless steel. To simplify the simulation, the microstructure was considerd to be homogeneous and the differences in the mechanical properties of the two constituent phases were neglected in the calculations.

Results

Computer simulation

The outer layer of the material, which is fully saturated with hydrogen, will have to undergo a linear expansion of approximately 6 %, which corresponds to a volume expansion of approximately 18 %. Since the bulk of the material restricts expansion parallel to the surface, most of this volume change is accommodated by an extension in the thickness direction, which causes considerable plastic strains. This effect takes place during the first few minutes of hydrogen charging. Right at the start of out gassing the opposite effect takes place. The out gassing layer has to undergo a negative volume change of approximately 18 %, which can only be accommodated by a contraction perpendicular to the surface of the specimen and a considerable plastic strain. This plastic straining is accompanied by an all-sided tensile stress parallel to the surface of the specimen.
The history of the calculated equivalent plastic strain in the outermost layer can be seen in fig.1. The sharp increase in equivalent plastic strain at the start of the hydrogen charging and at the beginning of out-gassing is clear in the simulations. The plastic deformation calculated in the depth of the material is shown in fig. 2. The plastic deformation is mostly localised in a layer of approximately 25 μm (fig. 2).

Experimental results

The experimental results support the indications obtained from the simulation. When hydrogen charging of the strip was started on one surface, as expected, the strip deflected and the hydrogen charged surface became convex. For the strip to bend without externally applied load, it is necessary that a compressive stress is present on the convex side. The bending of the strip after hydrogen charging clearly indicates that compressive stresses are set up on the surface as a result of the expansion of the surface due to hydrogen charging. During the experiment, the bending of the specimen was monitored by measuring the deflection of the tip of the strip. The results are shown in fig. 3. As is evident, there is a rapid initial deflection. The deflection rate then drops to a very low value. These results are in good agreement with the predicted deformation with time as seen in fig. 1. When charging was discontinued, the strip did not return to the original form. Some amount of deflection was retained.

Using X-ray diffraction, residual stress was measured on the surface subjected to hydrogen charging and out gassing. A residual all-sided tensile stress of 250 MPa was measured in the surface layer at the end of the charging - outgassing cycle. The computer simulation yielded an eventual value of 690 MPa. The surface of the specimen was then examined with SEM for a probable explanation of the difference. The results of the SEM examination can be seen in fig. 4. The surface is found to contain several cracks, which are visible at 5000 X. The cracks occur mainly in the austenite phase, while the ferrite shows some amount of twinning in the lower right of the picture.

Discussion

During the hydrogen charging cycle, the surface layer of the specimen undergoes severe plastic deformation. When compared to a tensile test, the deformation amounts to a cycle of first 18 % in compression, followed by an equal amount of deformation in tension. During the out gassing, the stress state in the surface layer is characterized by a biaxial tensile stress of up to 700 MPa. Assuming fracture to be dependent on the hydrostatic stress component, this biaxial stress magnitude corresponds to an improbable equivalent stress of 1400 MPa in a tensile test. The two phases in the duplex stainless steel show a characteristic difference in plastic accommodation. The ferrite phase has higher mechanical strength and hardness than the austenite phase. It is likely that stress is first accommodated by plastic deformation in the austenite, followed by the ferrite phase.

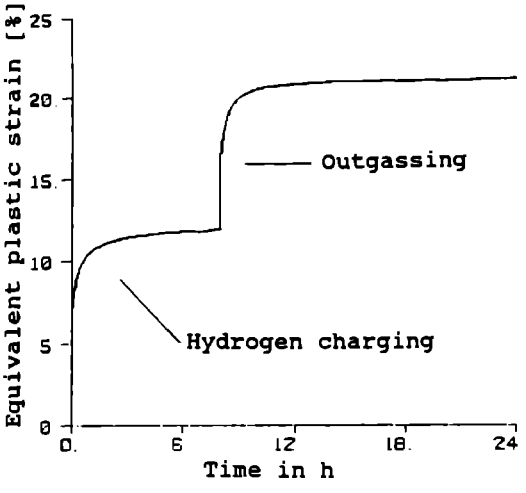

Fig.1
History of plastic strain

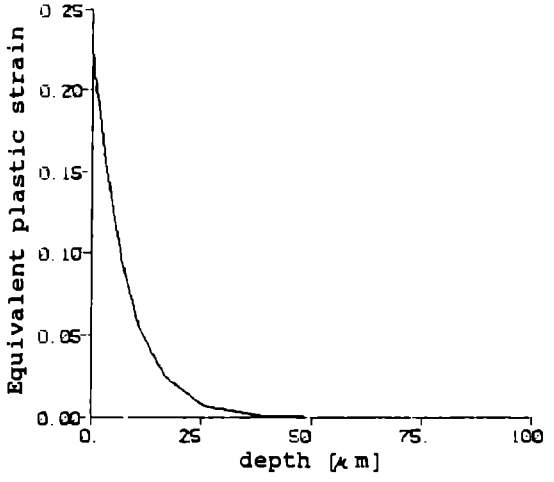

Fig.2
Plastic strain vs depth

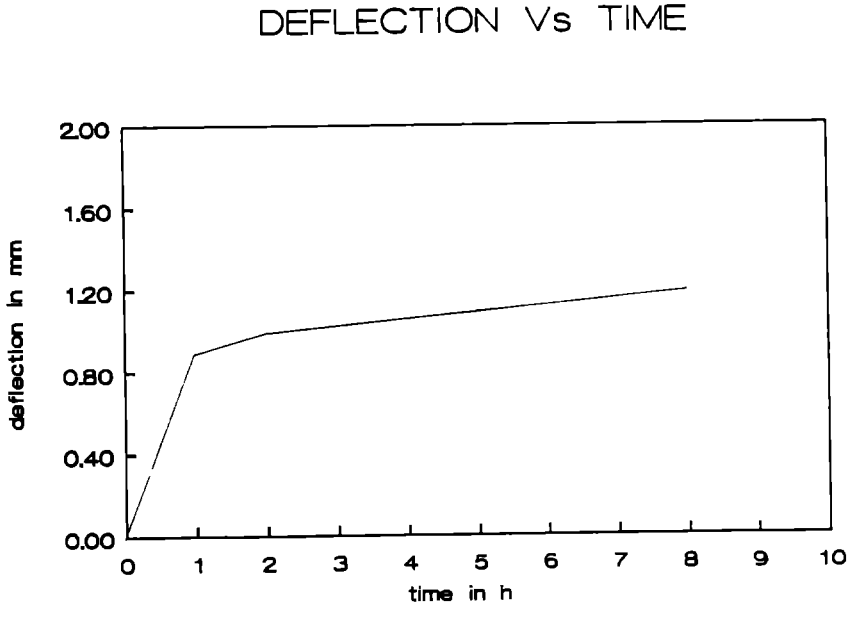

Fig. 3
Deflection vs time of charging

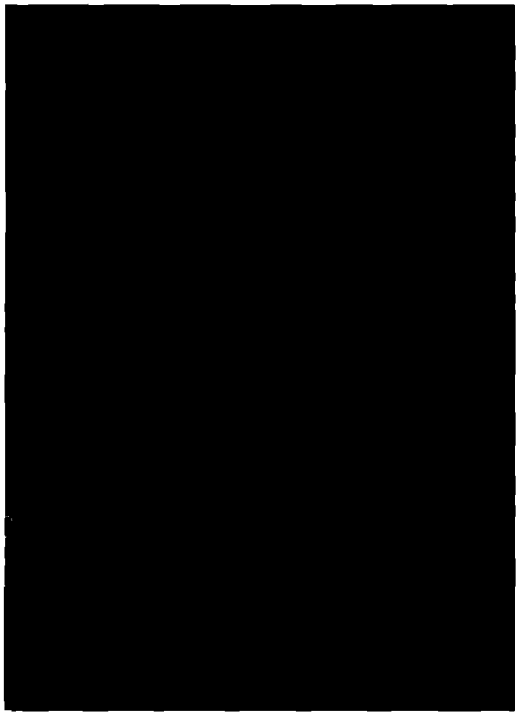

Fig. 4
SEM micrograph of specimen surface.

In our view the high tensile stresses, preceeded by severe plastic deformation, in the presence of hydrogen, are responsible for the cracks in the austenite grains on the surface layer of the specimen. The stress relaxation due to cracking accounts for the lower value of the residual stress found from X-ray diffraction as compared to the simulation. Elizier et al. have attributed the surface cracking to the severe plastic deformation produced by the hydrogen charging (12).

To our knowledge, quantitative analysis of the surface plastic deformation due to hydrogen charging is not found in the literature. The simulations reported here have shown that the accumulated plastic deformation, after charging and discharging, of the surface is of the order of 20 %.

In view of the above, it is interesting to consider several reports which have appeared in the literature (13-17) which suggest that hydrogen enhances the mobility and the generation of dislocations. Most of these studies have been conducted on thin foils which are charged with gaseous hydrogen. The present investigations clearly indicate that when hydrogen is introduced on the surface, the compressive stress generated by the expansion of the surface is high enough to cause plastic deformation. In a thin specimen of a few thousand angstroms, the surface strains, generated in a few seconds, can provide the driving force for the dislocation generation and movement. The concept of hydrogen induced dislocation mobility should be re examined.

Conclusions

1. Cathodic hydrogen charging leads to plastic deformation of the surface of duplex stainless steels
2. The plastic deformation of the surface in the presence of hydrogen leads to cracking of the austenite phase
3. Finite element analysis of the hydrogen charging and outgassing shows accumulated plastic deformation as high as 20 %
4. The strains introduced by hydrogen provide the driving force for the dislocation movement.

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